XXV. *On the Thermal Effects of Fluids in Motion.*—Part IV.
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In the Second Part of these researches we have given the results of our experiments on the difference between the temperatures of an elastic fluid on the high- and low-pressure sides of a porous plug through which it was transmitted. The gases employed were atmospheric air and carbonic acid. With the former, 0°·0176 of cooling effect was observed for each pound per square inch of difference of pressure, the temperature on the high-pressure side being 17°·125. With the latter gas, 0°·0833 of cooling effect was produced per lb. of difference of pressure, the temperature on the high-pressure side being 12°·844.

It was also shown that in each of the above gases the difference of the temperatures on the opposite sides of the porous plug is sensibly proportional to the difference of the pressures.

An attempt was also made to ascertain the cooling effect when elastic fluids of high temperature were employed; and it was satisfactorily shown that in this case a considerable diminution of the effect took place. Thus, in air at 91°·58, the effect was only 0°·014; and in carbonic acid at 91°·52, it was 0°·0474.

In the experiments at high temperatures there appeared to be some grounds for suspecting that the apparent cooling effect was too high; for the quantity of transmitted air was very considerable, and its temperature possibly had not arrived accurately at that of the bath by the time it reached the porous plug.

The obvious way to get rid of all uncertainty on this head was to increase the length of the coil of pipes. Hence in the following experiments the total length of 2-inch copper pipe immersed in the bath was 60 feet instead of 35, as in the former series. The volume of air transmitted in a given time was also considerably less. There could therefore be no doubt that the temperature of the air on its arrival at the plug was sensibly the same as that of the bath.

The nozle employed in the former series of experiments was of box-wood,—the space occupied by cotton-wool, or other porous material, being 2·72 inches long and an inch and a half in diameter. The box-wood was protected from the water of the bath by being enveloped by a tin can filled with cotton-wool. This was unquestionably in most respects the best arrangement for obtaining accurate results; but it was found necessary to make each experiment last one hour or more before we could confidently depend on the thermal effect. The oscillations of temperature which took place during the first

part of the time were traced to various causes, one of the principal being the length of time which, on account of the large capacity for heat and the small conductivity of the box-wood nozle, elapsed before the first large thermal effects consequent on the getting up of the pressure were dissipated. No doubt the results we arrived at were very accurate with the elastic fluids employed, viz. atmospheric air and carbonic acid; but we possessed an unlimited supply of the former and a supply of the latter equal to 120 cubic feet, which was sufficient to last for more than half an hour without being exhausted. In extending the inquiry to gases not so readily procured in large quantities, it was therefore desirable to use a porous plug of smaller dimensions enclosed in a nozle of less capacity for heat, so as to arrive rapidly at the normal effect.

Various alterations of the apparatus were made in order to meet the new requirements of our experiments. A small high-pressure engine of about one horse-power was placed in gear with a double-acting compressing air-pump, which had a cylinder $4\frac{1}{2}$ inches in diameter, with a length of stroke of 9 inches. The engine was able to work the piston of the pump sixty complete strokes in the minute. The quantity of air which it ought to have discharged at low pressure was therefore upwards of 16,000 cubic inches per minute. But much loss, of course, occurred from leakage past the metallic piston, and in consequence of the necessary clearance at the top and bottom of the cylinder when the pressure increased by a few atmospheres; so that in practice we never pumped more than 8000 cubic inches per minute.

The nozle we employed will be understood by inspecting Plate XXVI. fig. 1, where $a\,a$ is the upright end of the coil of copper pipes. On a shoulder within the pipe a perforated metallic disk ($b$) rests. Over this is a short piece of india-rubber tube ($c\,c$) enclosing a silk plug ($d$), which is kept in a compressed state by the upper perforated metallic plate ($e$). This upper plate is pressed down with any required force by the operation of the screw $f$ on the metallic tube $g\,g$. A tube of cork ($h\,h$) is placed within the metallic tube, in order to protect the bulb of the thermometer from the effects of a too rapid conduction of heat from the bath. Cotton-wool is loosely packed round the bulb, so as to distribute the flowing air as evenly as possible. The glass tube ($i\,i$) is attached to the nozle by means of a piece of strong india-rubber tubing, and through it the indications of the thermometer are read. The top of the glass tube is attached to the metallic tube $l\,l$, for the purpose of conveying the gas to the meter.

The thermometer ($m$) for registering the temperature of the bath is placed with its bulb near the nozle. The level of the water is shown by $n\,n$; and $o\,o$ represents the wooden cover of the bath.

When a high temperature was employed, it was maintained by introducing steam into the bath by means of a pipe led from the boiler. The water of the bath was in every case constantly and thoroughly stirred, especially when high temperatures were used.

The general disposition of the apparatus will be understood from fig. 2, in which A represents the boiler, B the steam-engine geared to the condensing air-pump C. From this pump the compressed air passes through a train of pipes 60 feet long and 2 inches

in diameter, and then enters the coil of pipes in the bath D. Thence, after issuing from the porous plug, it passes through the gasometer E, and ultimately arrives again at the pump C. This complete circulation is of great importance, inasmuch as it permits the gas which has been collected in the meter to be used for a much longer period than would otherwise have been possible. A glass vessel full of chloride of calcium is placed in the circuit at F, and chloride of calcium is also placed in the pipe at $f$. A small tube leading from the coil is carried to the shorter leg of the glass siphon gauge G, of which the longer leg is 17 feet, and the shorter 12 feet long.

The thermometers employed were all carefully calibrated, and had about ten divisions to the degree Centigrade. We took the precaution of verifying the air- and bath-thermometers from time to time, especially when high temperatures were used, in which latter case a comparison between the thermometers at high temperature was made immediately after each experiment.

## Atmospheric Air.

In the experiments described in the present paper, the air was not deprived of its carbonic acid. It was simply dried by transmitting it in the first place, before it entered the pump, through a cylinder 18 inches long and 12 inches in diameter filled with chloride of calcium, and afterwards, in its compressed state, through a pipe 12 feet long and 2 inches in diameter filled with the same substance. The experiments were principally carried on in the winter season; so that the chloride kept dry for a long time. From its condition after some weeks' use, it was evident that the water was removed, almost as much as chloride of calcium can remove it, after the air had traversed three inches of the chloride contained by the first vessel.

### TABLE I.

| No. of experiment. | Cubical inches of air transmitted per minute. | Pressure over that of the atmosphere, in inches of mercury. | Temperature of the bath. | Thermal effect. | Correction on account of conduction of heat. | Corrected thermal effect. | Thermal effect reduced to the pressure of 100 inches of mercury. | Time occupied by experiment, in minutes. | Number of observations comprised in each mean. | Extreme range of the temperature of the bath. | Extreme range of the temperature of the air. | Extreme range of the pressure. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3000 | 83·96 | 4·499 | −0·711 | −0·044 | −0·755 | −0·900 | 14 | 5 | 0·020 | 0·015 | 2·25 |
| 2 | 3600 | 136·19 | 6·112 | −1·11 | −0·058 | −1·168 | −0·858 | 24 | 7 | 0·017 | 0·055 | 1·7 |
| 3 | 2600 | 156·59 | 6·082 | −1·307 | −0·094 | −1·401 | −0·895 | 15 | 5 | 0·009 | 0·065 | 8·0 |
| 4 | 1750 | 139·58 | 7·471 | −1·137 | −0·122 | −1·259 | −0·902 | 24 | 15 | 0·006 | 0·19 | 5·3 |
| 5 | 2250 | 153·9 | 7·640 | −1·231 | −0·103 | −1·334 | −0·867 | 12·5 | 10 | 0·008 | 0·028 | 3·6 |
| 6 | 2300 | 159·3| | 8·546 | −1·252 | −0·102 | −1·354 | −0·850 | 18 | 20 | 0·017 | 0·105 | 3·0 |
| 7 | 2060 | 165·73 | 8·2 | −1·329 | −0·121 | −1·450 | −0·875 | 14 | 15 | 0·034 | 0·128 | 4·8 |
| 8 | 1500 | 129·73 | 8·72 | −1·019 | −0·127 | −1·146 | −0·883 | 8 | 9 | 0·008 | 0·135 | 2·9 |
| 9 | 5000 | 128·9 | 24·92 | −0·983 | −0·037 | −1·020 | −0·791 | 12 | 8 | 0·015 | 0·09 | 7·0 |
| 10 | 4600 | 122·8 | 27·81 | −0·874 | −0·036 | −0·910 | −0·741 | 26 | 15 | 0·029 | 0·064 | 0 |
| 11 | 5000 | 123·5 | 42·64 | −0·947 | −0·036 | −0·983 | −0·796 | 8 | 4 | 0·127 | 0·122 | 7·0 |
| 12 | 4800 | 137 | 43·54 | −0·943 | −0 037 | −0·980 | −0·715 | 6 | 3 | 0·02 | 0·02 | 0 |
| 13 | 5000 | 127·5 | 47·92 | −0·937 | −0·037 | −0·974 | −0·764 | 6 | 4 | 0·058 | 0·09 | 2·0 |
| 14 | 3700 | 147 | 49·96 | −0·969 | −0·049 | −1·018 | −0·692 | 35 | 30 | 0·14 | 0·26 | 0 |
| 15 | 5600 | 146 | 53·375 | −0·860 | −0·028 | −0·888 | −0·608 | 28 | 30 | 0·05 | 0·08 | 0 |
| 16 | 5700 | 146 | 64·9 | −0·870 | −0·029 | −0·899 | −0·616 | 24 | 20 | 0·18 | 0·23 | 0 |
| 17 | 2700 | 112·43 | 89·901 | −0·469 | −0·033 | −0·502 | −0·446 | 20 | 10 | 0·112 | 0·23 | 8·6 |
| 18 | 1700 | 147 | 90·353 | −0·821 | −0·091 | −0·912 | −0·620 | 4 | 3 | 0·022 | 0·085 | 0 |
| 19 | 1700 | 153·16 | 92·486 | −0·756 | −0·083 | −0·839 | −0·547 | 19 | 10 | 0·202 | 0·273 | 7·0 |
| 20 | 3150 | 156·5 | 92·603 | −0·674 | −0·040 | −0·714 | −0·456 | 12 | 10 | 0·078 | 0·19 | 3·5 |
| 21 | 3800 | 146 | 93·78 | −0·700 | −0·036 | −0·736 | −0·504 | 24 | 20 | 0·236 | 0·255 | 0 |
| 22 | 4600 | 158·5 | 97·528 | −0·722 | −0·029 | −0·751 | −0·474 | 20 | 16 | 0·112 | 0·115 | 0 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |

## Oxygen Gas.

This elastic fluid was procured by cautiously heating chlorate of potash mixed with a small quantity of peroxide of manganese. In its way to the meter it passed through a tube containing caustic potash, in order to deprive it of any carbonic acid it might contain. The same drying-apparatus was employed as in the case of atmospheric air.

### TABLE II.

| No. of experiment. | Cubical inches of elastic fluid transmitted per minute. | Composition of the elastic fluid. | Pressure over that of the atmosphere, in inches of mercury. | Temperature of the bath. | Thermal effect. | Correction on account of conduction of heat. | Corrected thermal effect. | Thermal effect reduced to the pressure of 100 inches of mercury. | Ditto, calculated for pure oxygen. | Time occupied by experiment, in minutes. | Number of observations comprised in each mean. | Extreme range of the temperature of the bath. | Extreme range of the temperature of the elastic fluid. | Extreme range of the pressure. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2000 | { 5·095 N / 94·905 O } | 159·28 | 8·682 | −1·547 | −0·145 | −1·692 | −1·061 | −1·075 | 9 | 10 | 0·007 | 0·35 | 7·8 |
| 2 | 2000 | { 54·62 N / 45·38 O } | 161·81 | 8·75 | −1·373 | −0·129 | −1·502 | −0·928 | −1·074 | 11 | 10 | 0·017 | 0·046 | 0·9 |
| 3 | 1700 | { 3·64 N / 96·36 O } | 151 | 89·466 | −1·069 | −0·118 | −1·187 | −0·786 | −0·800 | 14 | 10 | 0·45 | 0·43 | 6·2 |
| 4 | 3150 | { 22·37 N / 77·63 O } | 159·77 | 90·8 | −0·840 | −0·050 | −0·890 | −0·557 | −0·580 | 12 | 10 | 0·326 | 0·336 | 8·0 |
| 5 | 3150 | { 51·03 N / 48·97 O } | 154·1 | 92·792 | −0·734 | −0·043 | −0·777 | −0·504 | −0·527 | 12 | 10 | 0·18 | 0·19 | 4·0 |
| 6 | 4500 | { 4 N / 96 O } | 152 | 95·453 | −0·795 | −0·033 | −0·828 | −0·544 | −0·570 | 11 | 8 | 0·135 | 0·158 | 0 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |

## Nitrogen Gas.

In preparing this gas the meter was first filled with air, and then a long shallow tin vessel was floated under it, containing sticks of phosphorus so disposed as to burn in succession. Some hours were allowed to elapse after the combustion had terminated, in order to allow of the deposition of the phosphoric acid formed.

### TABLE III.

| No. of experiment. | Cubical inches of elastic fluid transmitted per minute. | Composition of the elastic fluid. | Pressure over that of the atmosphere, in inches of mercury. | Temperature of the bath. | Thermal effect. | Correction on account of conduction of heat. | Corrected thermal effect. | Thermal effect reduced to the pressure of 100 inches of mercury. | Ditto, calculated for pure nitrogen. | Time occupied by experiment, in minutes. | Number of observations comprised in each mean. | Extreme range of the temperature of the bath. | Extreme range of the temperature of the elastic fluid. | Extreme range of the pressure. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2050 | { 7·9 O / 92·1 N } | 163·38 | 7·204 | −1·448 | −0·133 | −1·581 | −0·967 | −1·034 | 7 | 8 | 0·008 | 0·25 | 6·2 |
| 2 | 2500 | { 2·2 O / 97·8 N } | 162·65 | 91·415 | −0·857 | −0·064 | −0·921 | −0·567 | −0·576 | 13 | 10 | 0·036 | 0·48 | 4·5 |
| 3 | 2500 | { 12·5 O / 87·5 N } | 164·61 | 91·965 | −0·869 | −0·065 | −0·934 | −0·567 | −0·691 | 12 | 9 | 0·337 | 0·378 | 3·0 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |

## Carbonic Acid.

This gas was formed by adding sulphuric acid to a solution of carbonate of soda. It was dried in the same manner as all the other gases.

## TABLE IV.

| No. of experiment. | Cubical inches of elastic fluid transmitted per minute. | Composition of the elastic fluid. | Pressure over that of the atmosphere, in inches of mercury. | Temperature of the bath. | Thermal effect. | Correction on account of conduction of heat. | Corrected thermal effect. | Thermal effect reduced to the pressure of 100 inches of mercury. | Ditto, calculated for pure carbonic acid, calling its sp. heat for equal vol. 1·39. | Time occupied by experiment, in minutes. | Number of observations comprised in each mean. | Extreme range of the temperature of the bath. | Extreme range of the temperature of the elastic fluid. | Extreme range of the pressure. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2450 | 68·42 Air / 31·58 $CO_2$ | 163·7 | 7·362 | −2·699 | −0·190 | −2·889 | −1·765 | −3·166 | 12 | 10 | 0 | 0·16 | 3·2 |
| 2 | 2350 | 89·16 Air / 10·84 $CO_2$ | 148·82 | 7·360 | −1·621 | −0·125 | −1·746 | −1·173 | −2·990 | 14 | 10 | 0·004 | 0·282 | 9·2 |
| 3 | 3100 | 3·52 Air / 96·48 $CO_2$ | 164·07 | 7·384 | −6·719 | −0·299 | −7·018 | −4·277 | −4·367 | 6·5 | 6 | 0·008 | 0·021 | 1·4 |
| 4 | 2500 | 62·5 Air / 37·5 $CO_2$ | 162·925 | 7·407 | −2·839 | −0·191 | −3·030 | −1·860 | −3·052 | 8 | 8 | 0·007 | 0·11 | 5·8 |
| 5 | 2300 | 88·13 Air / 11·87 $CO_2$ | 158·08 | 7·433 | −1·682 | −0·132 | −1·814 | −1·147 | −2·648 | 10 | 10 | 0·005 | 0·107 | 5·2 |
| 6 | 2260 | 97·46 Air / 2·54 $CO_2$ | 163·52 | 7·608 | −1·407 | −0·116 | −1·523 | −0·931 | −2·753 | 8 | 8 | 0·007 | 0·064 | 2·0 |
| 7 | 3300 | 4·0 Air / 5·286 H / 90·714 $CO_2$ | 161·97 | 7·960 | −6·131 | −0·262 | −6·393 | −3·947 | −4·215 | 6 | 8 | 0 | 0·18 | 4·8 |
| 8 | 3000 | 4·23 Air / 46·47 H / 49·3 $CO_2$ | 153·72 | 8·020 | −2·189 | −0·117 | −2·306 | −1·500 | −2·631 | 5 | 5 | 0 | 0·19 | 1·6 |
| 9 | 1500 | 7·09 Air / 67·05 H / 25·86 $CO_2$ | 97·56 | 8·296 | −0·543 | −0·063 | −0·606 | −0·622 | −1·940 | 15 | 15 | 0·012 | 0·146 | 5·4 |
| 10 | 2925 | 2·11 Air / 97·89 $CO_2$ | 167·25 | 93·523 | −3·418 | −0·160 | −3·578 | −2·139 | −2·164 | 10 | 10 | 0·382 | 0·49 | 4·0 |
| 11 | 2925 | 56·78 Air / 43·22 $CO_2$ | 167·4 | 91·26 | −1·746 | −0·099 | −1·845 | −1·102 | −1·674 | 30 | 20 | 0·292 | 0·49 | 11·0 |
| 12 | 2925 | 77·77 Air / 22·23 $CO_2$ | 146·83 | 91·642 | −1·292 | −0·077 | −1·369 | −0·938 | −2·053 | 9 | 6 | 0·045 | 0·245 | 3·5 |
| 13 | 5500 | 0·83 Air / 99·17 $CO_2$ | 146 | 54·0 | −4·184 | −0·104 | −4·288 | −2·937 | −2·951 | 24 | 16 | 0·24 | 0·46 | 0 |
| 14 | 5300 | 67·7 Air / 32·3 $CO_2$ | 147 | 49·703 | −1·832 | −0·059 | −1·891 | −1·286 | −2·225 | 24 | 16 | 0·025 | 0·17 | 0 |
| 15 | 5600 | 87·77 Air / 12·23 $CO_2$ | 145 | 49·764 | −1·250 | −0·032 | −1·282 | −0·884 | −2·025 | 20 | 16 | 0·01 | 0·11 | 0 |
| 16 | 5100 | 1·83 Air / 98·17 $CO_2$ | 127·5 | 35·604 | −4·186 | −0·112 | −4·298 | −3·371 | −3·407 | 18 | 15 | 0·03 | 0·095 | 0 |
| 17 | 5000 | 1·66 Air / 98·34 $CO_2$ | 151 | 97·553 | −3·11 | −0·084 | −3·194 | −2·115 | −2·135 | 20 | 16 | 0·292 | 0·272 | 0 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |

### Hydrogen.

Our method in procuring this elastic fluid was to pour sulphuric acid, prepared from sulphur, into a carboy nearly filled with water and containing fragments of sheet zinc. The gas was passed through a tube filled with rags steeped in a solution of sulphate of copper, and then through a tube filled with sticks of caustic potash. The rags became speedily browned, and we therefore adopted the plan of pouring a small quantity of solution of sulphate of copper from time to time into the carboy itself. This succeeded perfectly; the rags retained their blue colour, and the gas was rendered perfectly inodorous, whilst at the same time its evolution became much more free and regular.

## TABLE V.

| No. of experiment. | Cubical inches of elastic fluid transmitted per minute. | Composition of the elastic fluid. | Pressure over that of the atmosphere, in inches of mercury. | Temperature of the bath. | Thermal effect. | Correction on account of conduction of heat. | Corrected thermal effect. | Thermal effect reduced to the pressure of 100 inches of mercury. | Ditto, calculated for pure hydrogen. | Time occupied by experiment, in minutes. | Number of observations comprised in each mean. | Extreme range of the temperature of the bath. | Extreme range of the temperature of the elastic fluid. | Extreme range of the pressure. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3000 | {17·635 Air / 82·365 H} | 64·1 | 6·34 | −0·144 | −0·009 | −0·153 | −0·239 | −0·104 | 3 | 3 | 0 | 0 | 0 |
| 2 | 3000 | {75·16 Air / 24·84 H} | 99·86 | 6·355 | −0·564 | −0·035 | −0·599 | −0·600 | +0·226 | 10 | 4 | 0 | 0·15 | 1·5 |
| 3 | 3900 | {4·866 Air / 95·134 H} | 49·91 | 6·132 | +0·033 | +0·002 | +0·035 | +0·070 | +0·118 | 12 | 6 | 0·002 | 0·06 | 1·2 |
| 4 | 2900 | {78·295 Air / 21·705 H} | 99·657 | 5·808 | −0·535 | −0·034 | −0·569 | −0·571 | +0·525 | 34 | 12 | 0·03 | 0·11 | 1·85 |
| 5 | 2800 | {9·2 Air / 90·8 H} | 86·885 | 7·244 | +0·041 | +0·003 | +0·044 | +0·05 | +0·143 | 27 | 10 | 0·034 | 0·033 | 1·75 |
| 6 | 3300 | {1·798 Air / 98·202 H} | 79·84 | 7·572 | +0·043 | +0·003 | +0·046 | +0·058 | +0·075 | 23 | 8 | 0·008 | 0·023 | 2·85 |
| 7 | 2950 | {4·795 Air / 95·205 H} | 74·08 | 6·654 | +0·054 | +0·004 | +0·058 | +0·078 | +0·126 | 17 | 10 | 0·016 | 0·11 | 6·6 |
| 8 | 2650 | {67·75 Air / 32·25 H} | 130·97 | 6·717 | −0·571 | −0·040 | −0·611 | −0·466 | +0·383 | 12 | 6 | 0·01 | 0·07 | 2·6 |
| 9 | 3800 | {4·07 Air / 95·93 H} | 100·72 | 6·781 | +0·039 | +0·002 | +0·041 | +0·041 | +0·08 | 10 | 10 | 0·012 | 0·078 | 2·6 |
| 10 | 2700 | {58·29 Air / 41·71 H} | 144·02 | 6·846 | −0·504 | −0·035 | −0·539 | −0·375 | +0·317 | 8·5 | 8 | 0·011 | 0·07 | 3·6 |
| 11 | 1900 | {91·81 Air / 8·19 H} | 152·67 | 7·406 | −1·002 | −0·099 | −1·101 | −0·721 | +0·904 | 9 | 8 | 0 | 0·225 | 9·0 |
| 12 | 1760 | {97·56 Air / 2·44 H} | 138·55 | 7·474 | −1·032 | −0·11 | −1·142 | −0·825 | +0·814 | 13 | 8 | 0·001 | 0·053 | 8·2 |
| 13 | 3100 | {4·375 Air / 95·625 H} | 87·74 | 88·66 | +0·178 | +0·011 | +0·189 | +0·215 | +0·248 | 14 | 6 | 0·08 | 0·17 | 4·6 |
| 14 | 3300 | {6·08 Air / 93·92 H} | 91·52 | 92·951 | +0·081 | +0·005 | +0·086 | +0·094 | +0·132 | 18 | 8 | 0·157 | 0·07 | 3·2 |
| 15 | 3000 | {5·043 Air / 94·957 H} | 73·99 | 90·353 | +0·072 | +0·005 | +0·077 | +0·104 | +0·136 | 20 | 10 | 0·18 | 0·11 | 1·65 |
| 16 | 3000 | {2·99 Air / 97·01 H} | 85·15 | 89·242 | +0·111 | +0·007 | +0·118 | +0·139 | +0·159 | 42 | 15 | 0·472 | 0·44 | 3·2 |
| 17 | 2900 | {4·13 Air / 95·87 H} | 104·72 | 89·858 | +0·073 | +0·004 | +0·077 | +0·073 | +0·098 | 15·5 | 10 | 0·09 | 0·035 | 6·2 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |

### Remarks on the Tables.

The correction for conduction of heat through the plug, inserted in column 6 of Table I., and in column 7 of the rest of the Tables, was obtained from data furnished by experiments in which the difference between the temperature of the bath and the air was purposely made very great. It was considered as directly proportional to the difference of temperature, and inversely to the quantity of elastic fluid transmitted in a given time.

The 10th column of Tables II., III., IV., and V. is calculated on the hypothesis that, in mixtures with other gases, atmospheric air retains its thermal qualities without change. This hypothesis is almost certainly incorrect, since it is reasonable to expect that the effect of mixture on the physical character is experienced by each of the constituent gases. The column is given as one method of showing the effect of mixture.

*Effect of Mixture on the Constituent Gases.*—Although the experiments on nitrogen

given in Table III. are not so numerous as might be desired, we may infer from them, and the results in Table II., that common air and all other mixtures of oxygen and nitrogen behave more like a perfect gas, *i. e.* give less cooling effect than either one or the other gas alone. We might expect the mixture to be something intermediate between the two. But this does not appear to be the case. The two are very nearly equal in their deviations from the condition of a perfect gas. Nitrogen deviates less than oxygen, but oxygen mixed with nitrogen differs less than nitrogen!

In the case of carbonic acid, which at low temperatures (7°) deviates five times as much as atmospheric air, we might expect that a mixture of $CO_2$ and air would deviate more than air and less than $CO_2$. This is the case (see Table IV.). Further, we might expect the two to contribute each its proportion of cooling effect according to its own amount, and its specific heat volume for volume. But do the mixtures exhibit such a result? No! See column 10, Table IV., in which also note, under experiments 8 and 9, the great diminution produced by the admixture of hydrogen.

If, instead of attributing to air and carbonic acid moments in proportion to their specific heats, or $1 : 1\cdot39$, as we have done in column 10, we use $1 : \cdot7$, we obtain more consistent results.

Let $\delta$ denote the cooling effect experienced by air per 100 inches of mercury, $\delta'$ that by carbonic acid, and $\Delta$ that by a mixture of volume V of air, and V′ of carbonic acid; then we may take

$$\Delta = \frac{m\text{V}\delta + m'\text{V}'\delta'}{m\text{V} + m'\text{V}'}$$

to represent the cooling effect for the mixture, where $m$ and $m'$ are numbers which we may call the moments (or importances) of the two in determining the cooling effect for the mixture. The ratio of $m$ to $m'$ is the proper result of each experiment on a mixture, if we knew with perfect accuracy the cooling effect for each gas with none of the other mixed. Now for common air we have direct experiments (Table I.), and know the cooling effect for it better than from any inferences from mixtures. But for pure $CO_2$ we know the effect, for the most part, only inferentially. Hence, having tried making $m : m' :: 1 : 1\cdot39$ without obtaining consistent results, we tried other proportions; and, after various attempts, found that $m : m' :: 1 : \cdot7$, for all temperatures and pressures within the limits of our experiments, gives results as consistent with one another as the probable errors of the experiments justify us in expecting. Thus, using the formula

$$\Delta = \frac{\text{V}\delta + \text{V}'\delta' \times \cdot7}{\text{V} + \text{V}' \times \cdot7},$$

we have, for calculating the effect for $CO_2$ from any experiment on a mixture, the following formula,

$$\delta' = \frac{(\text{V} + \text{V}' \times \cdot7)\Delta - \text{V}\delta}{\text{V}' \times \cdot7}.$$

Hence, using the numbers in columns 3 and 9 of Table IV. which relate to mixtures of air and carbonic acid alone, we find

TABLE VI.

| No. of experiment. | Proportions of mixtures. | | Temperature of bath. | Thermal effect for air. | Deduced thermal effect for pure $CO_2$. |
|---|---|---|---|---|---|
| | Air. | $CO_2$. | | | |
| 1 | 68·42 | 31·58 | 7·36 | —·88 | —4·51 |
| 2 | 89·16 | 10·84 | 7·36 | —·88 | —4·61 |
| 3 | 3·52 | 96·48 | 7·38 | —·88 | —4·46 |
| 4 | 62·5 | 37·5 | 7·41 | —·88 | —4·19 |
| 5 | 88·13 | 11·87 | 7·43 | —·88 | —3·98 |
| 6 | 97·46 | 2·54 | 7·61 | —·88 | —3·89 |
| 16 | 1·83 | 98·17 | 35·6 | —·75 | —3·44 |
| 14 | 67·7 | 32·3 | 49·7 | —·7 | —3·04 |
| 15 | 87·77 | 12·23 | 49·76 | —·7 | —2·77 |
| 13 | 0·83 | 99·17 | 54 | —·66 | —2·96 |
| 10 | 2·11 | 97·89 | 93·52 | —·51 | —2·19 |
| 11 | 56·78 | 43·22 | 91·26 | —·51 | —2·21 |
| 12 | 77·77 | 22·23 | 91·64 | —·51 | —3·08 |
| 17 | 1·66 | 98·34 | 97·55 | —·49 | —2·16 |

|  1  |  2  |  3  |  4  |  5  |

The agreement for each set of results at temperatures nearly agreeing (with one exception, No. 12), shows that the assumption $m : m' :: 1 : \cdot 7$ cannot be far wrong within our limits of temperature.

[Received subsequently to the reading of the Paper.]

*Application of the preceding results to deduce approximately the Equation of Elasticity for the gases experimented on.*

The "equation of elasticity" for any fluid is the most appropriate name for the equation expressing the relation between the pressure and the volume of any portion of the fluid. As this relation depends on the temperature, the equation expressing it involves essentially three variables, which, as in our previous communications on this subject, we shall denote by $p$, $v$, $t$. Of these, $p$ is the pressure in units of force per unit of area, $v$ the volume of a unit mass of the fluid, and $t$ the temperature according to the absolute thermodynamic system of thermometry * which we have proposed. As before, we shall still adopt a degree, or thermometric unit, agreeing approximately with the degree Centigrade of the air-thermometer; according to which, as we have demonstrated by experiment †, the value of $t$ for the freezing-point is within a few tenths of a degree of 273·7 (its value at the standard boiling-point being, by definition of the Centigrade scale, 100° more than at the freezing-point).

Instead of, as in our previous communications, taking $v$ and $t$ as independent variables, we shall now take $p$ and $t$; and we shall accordingly consider the object of the equation of elasticity as being to express $v$ explicitly as a function of $p$ and $t$. Whatever may be the relation between these elements, the thermal effect, $d\vartheta$ (reckoned as positive when it is a rise in temperature), produced by forcing the fluid in a continuous stream through a narrow passage or porous plug by an infinitely small difference of pressures, $dp$, will

* Philosophical Transactions, 1854, p. 350.                    † Ibid. p. 352.

he given by the formula

$$\frac{d\vartheta}{dp} = -\frac{1}{JK}\left(t\frac{dv}{dt} - v\right),$$

where K denotes the thermal capacity, under constant pressure, of unit of mass of the fluid. This formula may be derived from equation (15.) of our previous communication already referred to, by substituting $p$, $v$, and $-\vartheta$ for P, V, and $\delta$ in that equation, changing to $p$ and $t$, instead of $v$ and $t$, as independent variables, and differentiating with reference to $p$. It is scarcely necessary to remark that a direct demonstration of our present formula, founded on elementary thermodynamic principles, may be readily obtained.

Each experiment, of the several series recorded above, gives a value for $\frac{d\vartheta}{dp}$, which is found by multiplying the "corrected thermal effect" by $\frac{\cdot299218}{2114}$, to reduce from the amounts per 100 inches of mercury to the amounts per pound per square foot. Now by examining carefully the series of results for different temperatures, in the cases of atmospheric air and of carbonic acid, we find that they follow very closely the law of varying inversely as the square of the absolute temperature (or temperature Centigrade with 273·7 added). Thus for air the formula

$$^{\circ}\cdot92 \times \left(\frac{273\cdot7}{t}\right)^2$$

and for carbonic acid

$$4^{\circ}\cdot64 \times \left(\frac{273\cdot7}{t}\right)^2$$

express, the former almost accurately, the latter with a deviation which we shall hereafter investigate, the results through the whole range of temperature for which the investigation has been carried out.

### Air.

| Temperature. | Actual cooling effect. | Theoretical cooling effect. |
| --- | --- | --- |
| ° | ° | ° |
| 0 | ·92 | ·92 |
| 7·1 | ·88 | ·87 |
| 39·5 | ·75 | ·70 |
| 92·8 | ·51 | ·51 |

### Carbonic acid.

| Temperature. | Actual cooling effect. | Theoretical cooling effect. |
| --- | --- | --- |
| ° | ° | ° |
| 0 | 4·64 | 4·64 |
| 7·4 | 4·37 | 4·4 |
| 35·6 | 3·41 | 3·63 |
| 54·0 | 2·95 | 3·23 |
| 93·5 | 2·16 | 2·57 |
| 97·5 | 2·14 | 2·52 |

4 L

We have not experiments enough to establish the law of variation with temperature of the thermal effect for the pure gases oxygen and nitrogen, or for any stated mixture of them other than common air; but there can be no doubt, from the general character of the results, that the same law will be about as approximately followed by them as it is by air.

Hence we may presume that in all these cases the cooling effect is very well represented by the formula

$$\frac{-d\vartheta}{dp} = A\left(\frac{273\cdot7}{t}\right)^2.$$

Comparing this with the general formula given above, we find

$$t\frac{dv}{dt} - v = AJK\left(\frac{273\cdot7}{t}\right)^2.$$

The general integral of this differential equation, for $v$ in terms of $t$, is

$$v = Pt - \tfrac{1}{3}AJK\left(\frac{273\cdot7}{t}\right)^2,$$

P denoting an arbitrary constant with reference to $t$, which, so far as this integration is concerned, may be an arbitrary function of $p$. To determine its form, we remark in the first place, in consequence of BOYLE's law, that it must be approximately $\frac{C}{p}$, C being independent of both pressure and temperature; and thus, if we omit the second term, we have two gaseous laws expressed by the approximate equation

$$v = \frac{Ct}{p}.$$

Now it is generally believed that at higher and higher temperatures the gases approximate more and more nearly to the rigorous fulfilment of BOYLE's law. If this is true, the complete expression for P must be of the form $\frac{C}{p}$, since any other would simply show deviation from BOYLE's law at very high temperatures, when the second term of our general integral disappears. Assuming then that no such deviation exists, we have, as the complete solution,

$$v = \frac{Ct}{p} - \tfrac{1}{3}AJK\left(\frac{273\cdot7}{t}\right)^2 p.$$

This is an expression of exactly the same form as that which Professor RANKINE found applicable to carbonic acid, in the first place to express its deviations from the laws of BOYLE and GAY-LUSSAC, as shown by REGNAULT's experiments, and which he afterwards proved to give correctly the law and the absolute amount of the cooling effect demonstrated by our first experiments on that gas[*].

That more complicated formulæ were found for the law of elasticity for common air both by Mr. RANKINE and by ourselves, now seems to be owing to an irreconcileability among the data we had from observation. The whole amounts of the devia-

* Philosophical Transactions, 1854, Part II. p. 336.

tions from the gaseous laws are so small, for common air, that very small absolute errors in observations of so heterogeneous a character as those of REGNAULT on the law of compression and on the changes produced by pressure in the coefficients of expansion, and our own on the thermo-dynamic property on which we have experimented, may readily present us with results either absolutely inconsistent with one another, or only reconcileable by very strained assumptions. It is satisfactory now to find, when we have succeeded in extending our observations through a considerable range of temperature, that they lead to so simple a law; and it is probable that the formula we have been led to by these observations alone, will give the deviations from BOYLE's law, and the changes produced by pressure in the coefficients of expansion, with more accuracy than has hitherto been attained in attempts to determine these deviations by direct observation. We must, however, reserve for a future communication the comparison between such results of our theory and experiments and REGNAULT's direct observations. In the mean time we conclude by putting the integral equation of elasticity into a more convenient form, by taking $C = \dfrac{\mathfrak{H}}{t_o}$, where $\mathfrak{H}$ denotes the " height of the homogeneous atmosphere " for the gas under any excessively small pressure, at any temperature $t_o$, and taking $t_o$ to denote the absolute temperature of freezing water, in which case we shall have, as nearly as observations hitherto made allow us to determine,

$$t_o = 273^\circ \cdot 7.$$

Then, in terms of this notation, and of that above explained, in which $t$, $p$, $v$ denote absolute temperature, pressure in pounds weight per square foot, and volume in cubic feet of one pound of air, the equation of elasticity investigated above becomes

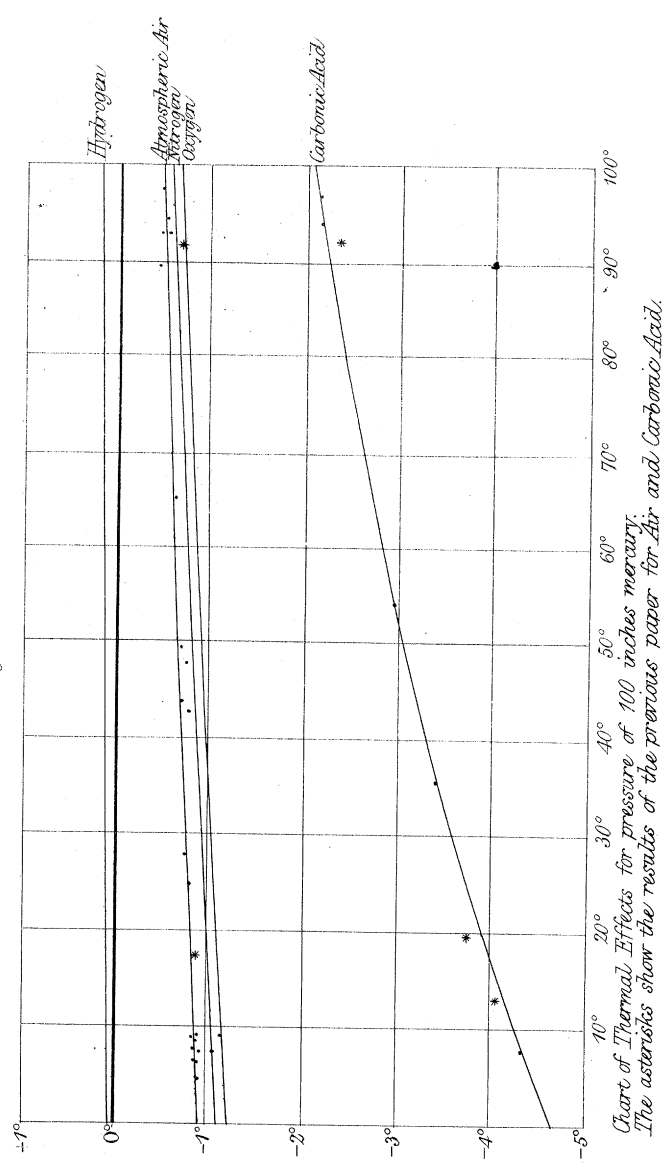$$v = \frac{\mathfrak{H}t}{pt_o} - \tfrac{1}{3}\text{AJK}\left(\frac{t_o}{t}\right)^2,$$

where A denotes the amount of the thermal effect per pound per square foot, determined by our observations, reckoned positive when it is a depression of temperature.
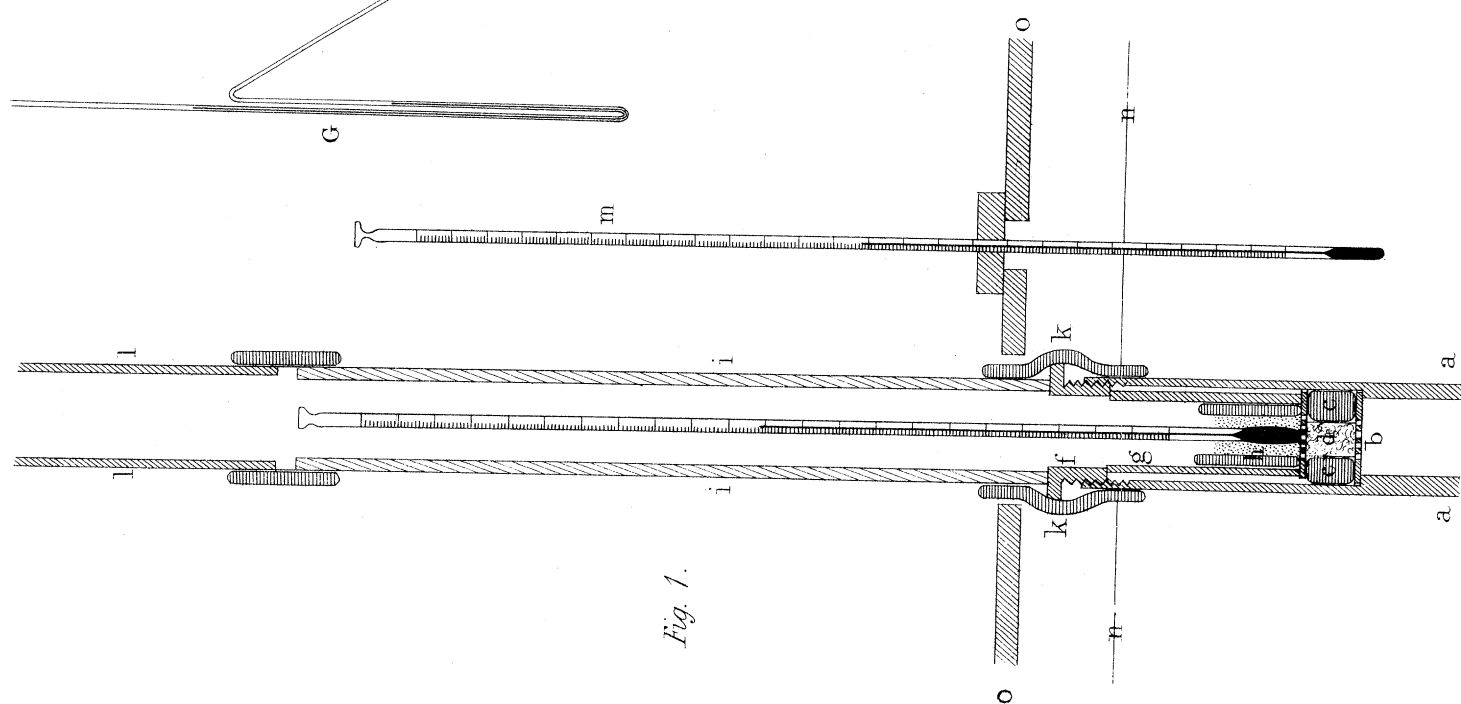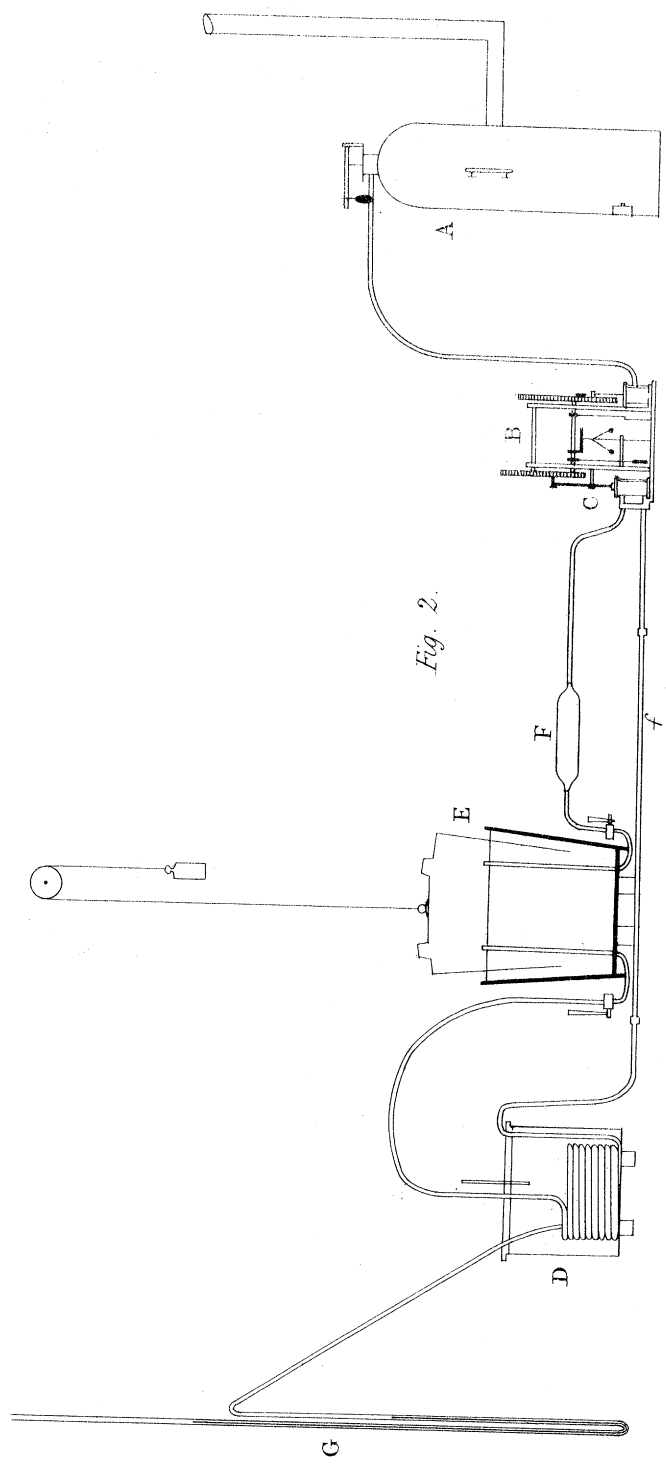
*Fig. 2.*

*Fig. 3.*

*Chart of Thermal Effects for pressure of 100 inches mercury.*

*The asterisks show the results of the previous paper for Air and Carbonic Acid.*

Hydrogen

Atmospheric Air

Nitrogen

Oxygen

Carbonic Acid

*Fig. 1.*